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Effect of Trivalent Chromium Based Treatment on the Protective Properties of Steel Coated with Polymeric Film

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Three main requirements are mandatory in order to achieve optimal quality in canned food: adequate processing of the product, definition of the preserving method, and a correct alloy for the deposit. Lacquer coatings are applied on food cans to enhance corrosion protection and also with decorative purposes. In this investigation, steel coated with a Cr³⁺ based treatment layer and polyethylene terephthalate polymeric film (PET), applied by co-extrusion, was characterized by electrochemical impedance spectroscopy (EIS) measurements, in NaCl 0.5 M solution, to evaluate the coating corrosion resistance in this environment. The experimental results showed that this new material (tin free) has good corrosion resistance regardless of the porosity found in the polymeric film, indicating that it can be a non-polluting alternative to replace tinplate and hexavalent chromium conversion layer in the food industry, being compatible with the packed product.

Introduction

The corrosion process of tinplate is complex due to the stratified structure and heterogeneity of the material (1). Moreover, to enhance its protective properties, a chromate passivation layer, which contains carcinogenic Cr⁶⁺ ions in the bath composition, is applied.

During 1980s electrolytic chromium coated steel (ECCS) was developed as an alternative to tinplate in lacquered applications (2). ECCS has a very thin layer of chromium/chromium oxide, approximately 10-15 nm, instead of 1 mm typical of tin layers (2). The oxide layer present on the metallic surface is responsible for the intermolecular forces with functional groups of the polymer (3).

Polymeric-coated steels are being developed for applications in the automotive industry as well as for food containers. For these applications, the main required properties are: good adhesion, enhanced barrier properties against water uptake and high corrosion resistance. However, it is documented that the protective ability of polymeric films depends on their physical-chemical characteristics as well as on the surface characteristics of their substrates (4).

Recently, new types of coating for ECCS-based packaging materials have been investigated. These coatings are thermoplastic layers like polyethylene terephthalate (PET) and polypropylene (PP) that are applied either through film coating or through a direct extrusion process in which a thin layer is extruded onto the ECCS substrate. These materials offer an extremely good formability in combination with other advantages in the process route (e.g. no solvent emissions) (2). Besides the thermoplastic layers, Cr³⁺ based treatment has been evaluated (5).

The adhesion properties of lacquered tinplate cans have been investigated by several authors (6, 7). Barilli et al (6) obtained good dry and wet adhesion with organosol and epoxyphenolic lacquers applied on tinplate, while Fragni et al (7) found that a post-curing thermal treatment provides a new less expensive way of improving the adhesion properties of cycloaliphatic epoxide-based UV lacquer system applied onto the tinplate substrate.

Electrochemical impedance spectroscopy (EIS) is a useful method to study the corrosion performance of polymer-coated metals. Many examples can be found in the literature that illustrate the use of EIS for comparing the performance of different coatings on metals (8-10), in particular for packaging steel.

The aim of the present work is to characterize the protective action of steel passivated by Cr³⁺ based electrolyte and coated with polyethylene terephthalate polymeric film (PET).

Experimental

The substrate used in this study consisted of electrolytic chromium coated steel (ECCS) plates, to which a polyethylene terephthalate (PET) copolymer (50 mm) was applied by colamination procedure. The coating morphology was observed by scanning electron microscopy (SEM).

Electrochemical impedance measurements were accomplished with a Solartron 1260 Frequency Response Analyzer (FRA) coupled to a 1296 Solartron dielectric interface connected to a computer. The amplitude of the perturbation signal was 10 mV (rms) and the frequency range studied from 10⁻² Hz a 10⁵ Hz, with an acquisition rate of 10 points per decade. The electrochemical cell consisted of a classic three-electrode arrangement; the counter electrode was a platinum sheet, a saturated calomel electrode (SCE) was used as a reference and the sample was the working electrode. All measurements were performed at room temperature in 0.5 M NaCl solution. All impedance measurements were carried out in a Faraday cage in order to minimize external interference on the system studied.

Results

Figure 1 presents a high magnification SEM image of the PET coated ECCS surface. The chromium coating exhibits a roughness microstructure, which must improve the adhesion between the PET coating and the chromate steel

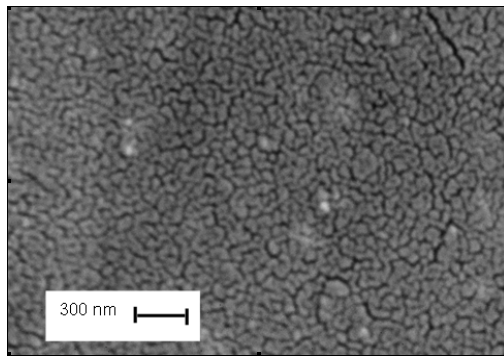


Figure 1: Secondary electrons SEM image of the PET coated ECCS steel.

EIS measurements were carried out until the appearance of corrosion products on the samples surface. The results are presented in the Figure 2.

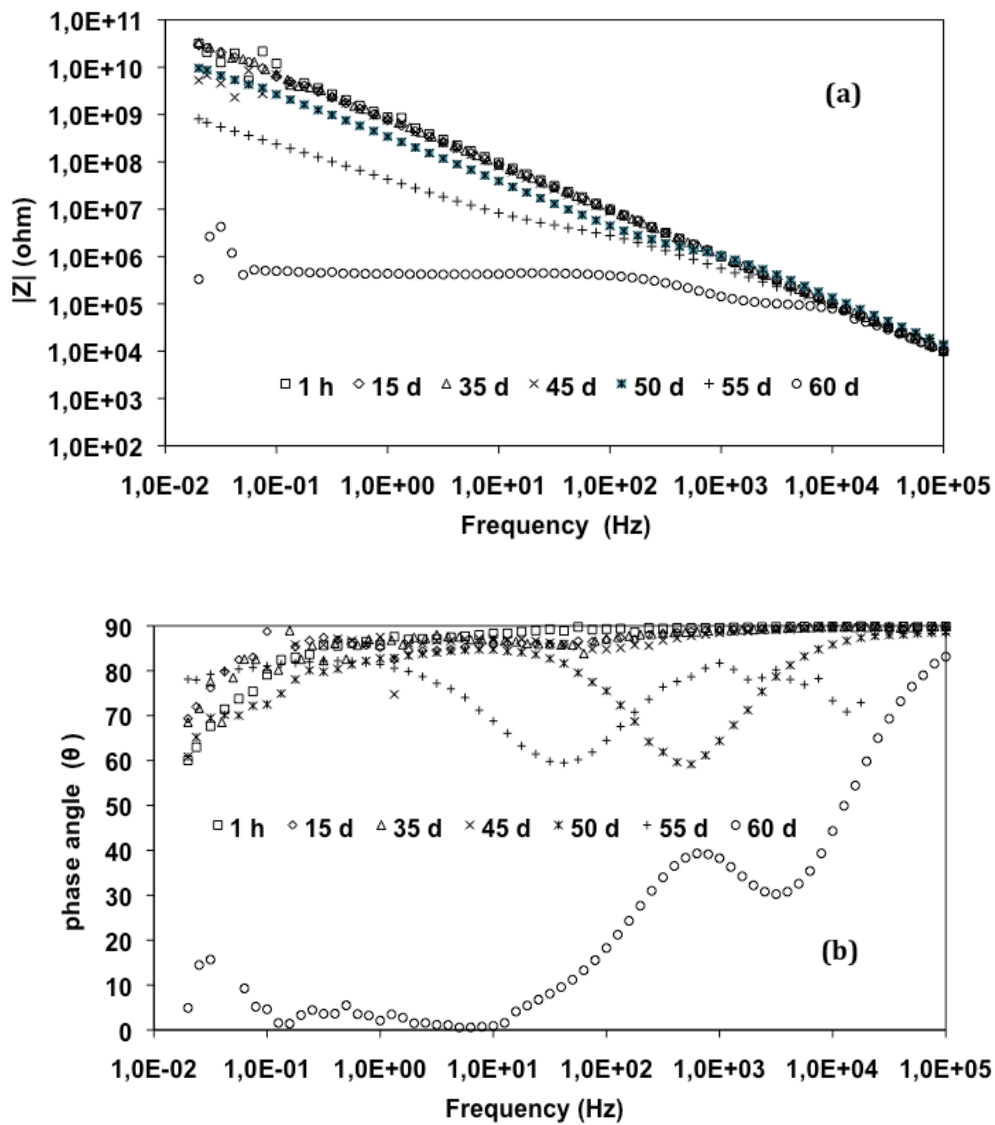


Figure 2: This figure presents the (a) Bode magnitude and (b) phase angle plots as a function of immersion time in 0.5 M solution for PET coated ECCS steel.

Figure 2 (a) shows the Bode plot of impedance modulus as a function of immersion time in the test solution for PET coated ECCS steel. A capacitive behavior is observed, (Figure 2(b)), and impedance values of about $10^{11} \Omega \cdot \text{cm}^2$ at low frequency. These values remain without significant changes with exposure time up to 50 days when they decay to values of $10^9 \Omega \cdot \text{cm}^2$. Impedance modulus at low frequencies is related to the corrosion resistance of the overall system, and when they do not change during immersion time this suggests that the surface do not suffer modification in this period. After 50 days of test, the decreasing impedance values suggest an electrochemically active interface. This is confirmed by the phase angle changes. Initially, Figure 2 (b) exhibits a maximum close to 89° , with a purely capacitive response, however after 50 days, new time constants are visible indicating the surface degradation.

In previous work (11), the average pore diameter of PET applied on ECCS steel, obtained by gas adsorption technique in a BET (Brunauer-Emmett-Teller) device, was 30 \AA , with variations of pore volume from 0,001 to 0,009 cm^3/g . These results indicate small defects on surface and a continuous polymeric film was obtained. Considering the polymeric film continuity and the EIS response, an excellent barrier was achieved.

Conclusions

The Cr^{3+} based electrolyte improves the adhesion between the PET coating and the steel. Consequently, the PET-coated ECCS plate provides an excellent protection barrier for the base steel, due to its surface continuity and regularity.

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